Pr environment			
Pr(1)—O(7) × 2	2.530 (10)		
Pr(1)—O(10) × 2	2.659 (12)		
Pr(1)—O(20) × 2	2.664 (8)		
Pr(1)—O(8) × 2	2.671 (8)		
Pr(1)—O(1) × 2	2.737 (11)		
Pr(1)—O(3) × 2	2.913 (8)		
Pr(2)—O(12)	2.420 (7)	Pr(2)—O(16)	2.763 (12)
Pr(2)—O(5)	2.452 (8)	Pr(2)—O(15)	2.903 (10)
Pr(2)—O(19)	2.468 (11)	Pr(2)—O(21)	2.951 (7)
Pr(2)—O(18)	2.504 (11)	Pr(2)—O(9)	2.981 (8)
Pr(2)—O(17)	2.589 (8)	Pr(2)—O(14)	3.033 (10)
Pr(2)—O(4)	2.701 (13)	Pr(2)—O(13)	3.198 (8)

Data were corrected for Lorentz–polarization and an empirical absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to isotropically refined data. Refinements of the occupancy factors for the Pr and Mo sites confirmed that they are fully occupied.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Structure solution and subsequent difference Fourier syntheses: *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Molecular graphics: *ORTEP*II (Johnson, 1976). Other calculations: *MolEN* (Fair, 1990). Computer: Digital MicroVAX 3100.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1118). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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σ-Dibarium Pyrophosphate

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Abstract

σ-Dibarium diphosphate, $Ba_2P_2O_7$, crystallizes in space group $P\bar{6}2m$ with the Ba atoms, separated by 4.703 Å, arranged in columns. Ba atoms are in sites of eleven- and tenfold coordination with Ba(1)—O and Ba(2)—O distances in the ranges 2.776 (8)–2.869 (6) and 2.878 (9)–3.080 (9) Å, respectively. One Ba atom has three interactions with bridging O atoms. P_2O_7 groups have threefold axes passing through the P atoms. The bridging O atom is disordered about these axes, with P—O—P angles of 130 (1) and 134 (4)°.

Comment

Historically, diphosphates of the $A_2P_2O_7$ type, in which A is a divalent cation, have been considered to exist as two types of structure predicated by the ionic radius of A, *i.e.* when the radius of A is less than 0.97 Å, the structure is of the thortveitite type, in which P_2O_7 groups display a staggered conformation (A = Mg, Mn, Fe, Co, Ni, Cu, Zn), and when the radius of A is greater than 0.97 Å (A = Ca, Sr, Ba, Pb), the diphosphate is seen to be in an eclipsed conformation (Brown & Calvo, 1970) and is categorized as the dichromate type.

Compounds of both types have been found to exist in allotropic forms. Thortveitite structures typically show a transition at temperatures below 873 K from a low-temperature or α form to a high-temperature or β form. Heating leads to a cell volume one quarter that of the ambient temperature form (one half in the case of Cu) and a more symmetrical structure. Typically, α forms show A atoms in layers, with AO_5 and AO_6 polyhedra sharing edges to form an irregular or 'broken-sided' two-dimensional array of hexagons. High-temperature forms are observed in space group $C2/m$ and show a regularization of the hexagon with the introduction of axial distortions in bonds to A. Cu (Robertson & Calvo, 1967, 1968), Co (Krishnamachari

& Calvo, 1972; ElBelghitti, Boukhari & Holt, 1994), Ni (Łukaszewicz, 1967; Pietraszko & Łukaszewicz, 1968), Mg (Calvo, 1965*a*, 1967) and Zn (Robertson & Calvo, 1970; Calvo, 1965*b*) all follow this pattern, with Ni showing a further transition to a σ form in which octahedral Ni atoms with little or no axial distortion form planes of regular hexagons (Masse, Guitel & Durif, 1979). Fe (Stefanidis & Nord, 1982; Hoggins, Swinnea & Steinfink, 1983) and Mn (Stefanidis & Nord, 1984) are known in only one form.

Dichromate-type structures require temperatures in excess of 975 K to effect a transition. For Sr and Ca, the known low-temperature forms are called β forms and crystallize in space group $P4_1$ (Hoffman & Mooney, 1960; Corbridge, 1957; Webb, 1966). β-$Sr_2P_2O_7$ is known only in powder form. Heating these isostructural β forms produces a transition to the α forms in space group *Pbnm* for Sr (Grenier & Masse, 1967; Hagman, Jansson & Magneli, 1968) or $P2_1/a$ for Ca (Calvo, 1968), with a halving of the cell volume and a decrease in density. The crystal structures of the two α forms are very similar, differing only in the obedience of P_2O_7 to internal mirror symmetry for α-$Sr_2P_2O_7$ and the absence of this mirror plane in the β-$Ca_2P_2O_7$ structure.

For Ca, both α and β structures show Ca atoms in pairs, separated by 3.85 and 3.68 Å, respectively. The Ca coordination changes from mixed seven-, eight- and ninefold to eightfold upon heating and the P_2O_7 groups retain their eclipsed conformation.

$Ba_2P_2O_7$ is reported to exist in two forms [α (*Pbnm*) with V = 727 Å^3 and σ ($P6_3$) with V = 543.35 Å^3], with a transition temperature of 1000 K. The National Bureau of Standards (1979) reported the powder pattern for the higher temperature form indexed according to space group $P6_3$. Below 1000 K, an α form isotypical with high-temperature or α-$Sr_2P_2O_7$ is reported (McCauley & Hummel, 1968; Ranby, Mash & Henderson, 1955; Mehdi, Hussain & Rao, 1977). Thus, the designation of the hexagonal form of $Ba_2P_2O_7$ as σ indicates that this is a higher temperature form than the α forms seen in all three alkaline earth metals. There are no reported single-crystal structures of either σ or α forms of $Ba_2P_2O_7$. The powder pattern of α-$Ba_2P_2O_7$ is reported to index according to orthorhombic symmetry (Mehdi, Hussain & Rao, 1977). There is no mention of the existence of a β form. We have determined the single-crystal structure of σ-$Ba_2P_2O_7$ in space group $P\bar{6}2m$ and found it to be unlike the known forms of other $A_2P_2O_7$ compounds.

Disorder of the bridging O atoms [O(11) and O(21)] about the threefold axes passing through P(1) and P(2) is seen. Bridging O atoms were refined with one third the occupancy appropriate for their sites [1/3 of 0.25 for O(11) and 1/3 of 0.5 for O(21)]. However, the U_{eq} values, anisotropic displacement parameters and errors in bonding details associated with these positions reflect disorder.

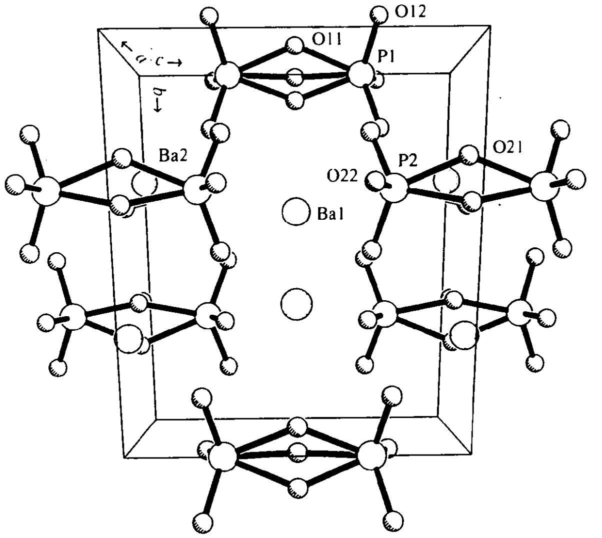

Fig. 1. Projection view of σ-dibarium diphosphate down the a axis showing the disorder of the bridging O-atom position.

Experimental

Crystals of $Ba_2P_2O_7$ were synthesized by fusion as follows:

$$2BaCO_3 + 2(NH_4)_2HPO_4 \rightarrow Ba_2P_2O_7 + 4NH_3\uparrow + 2CO_2\uparrow + 3H_2O\uparrow.$$

A 10% excess of $(NH_4)_2HPO_4$ was used. The mixture of starting materials was heated progressively to 1375 K and then cooled slowly (5 K h^{-1}) to ambient temperature yielding colorless crystalline material.

Crystal data

$Ba_2P_2O_7$
M_r = 448.6
Hexagonal
$P\bar{6}2m$
a = 9.415 (1) Å
c = 7.078 (1) Å
V = 543.4 (1) Å^3
Z = 3
D_x = 4.113 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 45 reflections
θ = 11.0–17.0°
μ = 11.234 mm^{-1}
T = 298 K
Chunk
0.2 × 0.2 × 0.2 mm
Colorless

Data collection

Syntex *P*4 four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1989)
T_{min} = 0.547, T_{max} = 0.698
1552 measured reflections
595 independent reflections
563 observed reflections [$F > 4.0\sigma(F)$]

R_{int} = 0.0388
θ_{max} = 30°
$h = -1 \rightarrow 11$
$k = -13 \rightarrow 1$
$l = -1 \rightarrow 9$
3 standard reflections monitored every 97 reflections intensity decay: negligible

Refinement

Refinement on F
$R = 0.0254$
$wR = 0.0333$
$S = 0.90$
563 reflections
41 parameters
$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{\max} = 1.263$
$\Delta\rho_{\max} = 2.07$ e Å^{-3}
$\Delta\rho_{\min} = -1.38$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ba(1)	0.3822 (1)	x	1/2	0.016 (1)
Ba(2)	0.2888 (1)	0	0	0.019 (1)
P(1)	0	0	0.2871 (5)	0.017 (1)
P(2)	2/3	1/3	−0.7835 (3)	0.018 (1)
O(12)	−0.1528 (8)	0	0.2314 (16)	0.053 (4)
O(22)	0.5112 (8)	0.1880 (7)	−0.7212 (12)	0.071 (3)
O(11)†	−0.076 (2)	0	1/2	0.024 (11)
O(21)†	0.374 (6)	−0.372 (6)	0	0.07 (2)

† Occupancy = 0.33.

Table 2. *Selected geometric parameters* (Å, °)

Ba(1)—O(12$^{\rm i}$)	2.878 (9)	Ba(2)—O(12$^{\rm vii}$)	2.869 (6)
Ba(1)—O(12$^{\rm ii}$)	2.878 (9)	Ba(2)—O(12$^{\rm xi}$)	2.869 (6)
Ba(1)—O(22$^{\rm iii}$)	3.080 (9)	Ba(2)—O(22$^{\rm iii}$)	2.776 (7)
Ba(1)—O(22$^{\rm iv}$)	2.893 (7)	Ba(2)—O(22$^{\rm xiii}$)	2.776 (7)
Ba(1)—O(22$^{\rm v}$)	3.080 (9)	Ba(2)—O(22$^{\rm xiv}$)	2.776 (8)
Ba(1)—O(22$^{\rm vi}$)	2.893 (7)	Ba(2)—O(22$^{\rm xv}$)	2.776 (8)
Ba(1)—O(22$^{\rm vii}$)	3.080 (9)	Ba(2)—O(21$^{\rm xvi}$)	2.86 (7)
Ba(1)—O(22$^{\rm viii}$)	2.893 (7)	Ba(2)—O(21$^{\rm xvii}$)	2.86 (6)
Ba(1)—O(22$^{\rm ix}$)	3.080 (9)	P(1)—O(12)	1.492 (8)
Ba(1)—O(22$^{\rm x}$)	2.893 (7)	P(1)—O(11)	1.666 (10)
Ba(1)—O(11$^{\rm xi}$)	2.89 (2)	P(2)—O(22)	1.485 (5)
Ba(2)—O(12$^{\rm xii}$)	2.869 (6)	P(2)—O(21$^{\rm xviii}$)	1.66 (3)
Ba(2)—O(12$^{\rm i}$)	2.869 (6)		
P(1)—O(11)—P(1$^{\rm xix}$)	130 (1)	P(2$^{\rm xiv}$)—O(21)—P(2$^{\rm xx}$)	134 (4)

Symmetry codes: (i) $-x, -x+y, z$; (ii) $-x, -x+y, 1-z$; (iii) $x, y, 1+z$; (iv) $1-x+y, 1-x, 1+z$; (v) $x, y, -z$; (vi) $1-x+y, 1-x, -z$; (vii) $y, x, -z$; (viii) $1-x, 1-x+y, -z$; (ix) $y, x, 1+z$; (x) $1-x, 1-x+y, 1+z$; (xi) $-x, -x+y, -z$; (xii) y, x, z; (xiii) $x, y, -1-z$; (xiv) $x-y, -y, -1-z$; (xv) $x-y, -y, 1+z$; (xvi) $-y, x-y-1, z$; (xvii) $1-x, 1-x+y, z$; (xviii) $1+y, x, z-1$; (xix) $x, y, 1-z$; (xx) $y, x-1, 1+z$.

A variable scan rate was used with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ to a maximum 2θ value of 60°. Refinement was completed using full-matrix least-squares methods.

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXS*86. Molecular graphics: *XP* (Siemens, 1990).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1095). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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